

SHOTTL'VOVA, E.A.; SYRKIN, Ya.K.

Dipole moments of organic azides. Doklady Akad. Nauk S.S.S.R. 87,
639-41 '52. (MJRA 5:11)
(GA 47 no.13:6203 '53)

1. Institut tonkoy khimicheskoy tekhnologii imeni M.V. Lomonosova,
Moscow.

NAZAROVA, L.M.; SYRKIN, Ya.K.

Dipole moments of some derivatives of furan and thiophene. Zhur.
Obshchey Khim. 23, 478-81 '53. (MLRA 6:3)
(CA 47 no.16:7847 '53)

1. L.Ya. Karpov Phys.-Chem. Inst., Moscow.

Syrkin, A. N.

Equivalence of bonds in quaternary ammonium compounds. L. M. Nazarov, M. G. Shchegolev and Ya. K. Syrkin. *Doklady Akad. Nauk S.S.S.R.* 90:1045-6 (1963).

All 4 bonds N—C in R_4N^+ are equiv., as shown by the following expts. with C^{14} -labelled MeI, Me_3N and labelled MeI (derived from labelled HCO_2Me) yielded labelled Me_4NI , which was thermally decompd. 30 hrs. at 250° in a N stream, the Me_3N being recovered in H_3PO_4 while the evolved MeI was treated with unlabelled Me_3N and the resulting Me_4NI examd. for C^{14} activity. Preliminary tests showed no recombination of Me_3N and MeI during the decompn. of the initial salt and that no Me group exchange occurs between MeI and Me_3N in H_3PO_4 . The C^{14} activity of the MeI evolved in the thermal decompn. was precisely 0.25 of the activity of the labelled quaternary salt. When Me_3NPhI , prepd. from Me_3NPh and labelled MeI, was decompd. at 170° , the resulting MeI after reaction with ordinary Me_3NPh gave a quaternary salt whose activity was 0.33 of that of the initial salt, thus again showing equivalence of the C—N links. G. M. K.

SYRKIN, Ya. K.

Diamagnetic susceptibilities of some organic compounds.
M. A. Lufanova and Ya. K. Syrkina (M. V. Lomansov
Inst. Fine Chem. Technol., Moscow); Izvest. Akad. Nauk
S.S.S.R., Otdel. Khim. Nauk 1954, 350-1.—The technique
described previously (cf. C.A. 49, 7277g) was used for detn.
of diamagnetic susceptibilities ($\times 10^{-9}$) of the following
compds.: 1-C₆H₅OH 95.23; 2-C₆H₅OH 98.25; 1-C₆H₅-
NH₂ 91.85; 2-C₆H₅NH₂ 93.60; 1-C₆H₅Me 102.15; 2-
C₆H₅Me 108.33; 1-C₆H₅NO₂ 98.47; 2-C₆H₅SO₂Cl 121.91;
2-C₆H₅SO₂NH₂ 127.6; o-O₂NC₆H₄NH₂ 67.64, m-isomer,
59.77, p-isomer 63.38; o-O₂NC₆H₄OH 68.97, m-isomer
65.91; p-C₆H₄Cl₂ 81.73; p-C₆H₄Cl 99.42; p-MeC₆H₄I
101.31; CO(NHPh), 134.05; PhNHCONHC₆H₄NO₂-m
148.1; PhNHCONHC₆H₄Me-o 164.0. The 2-derivs. have
higher susceptibilities than do the 1-analogs and the exptl.
values do not agree with the additive constns.
G. M. Kosolapoff—

Syrkin, Ya. K.

Dipole moments of some organic molecules. E. A. Shostakova and Ya. K. Syrkin (M. V. Lomonosov Inst. Fine Chem. Technol., Moscow). *Izvest. Akad. Nauk S.S.S.R., Khim. Nauk* 1954, 361-2. — Dipole moments of org. compds. were obtained by the heterodyne method in CH_2Cl_2 solns. at 25°; the solns. were generally 0.01-0.05 M. The following values of P_{tot} (total polarization), P_e (electronic polarization), and μ (in D.) were found: 4-cyclohexyloxy-pyridine 300.0, 51.33, 3.48; 4-phenoxy-pyridine 181.2, 47.03, 2.54; $\text{PhOCH}_2\text{CH}_3$ 62.83, 37.63, 1.1; $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3$ 79.53, 49.53, 1.2; $\text{BuOCH}_2\text{CH}_3$ 125.90, 36.42, 2.07; 1,1-azonaphthalene 98.27, 91.12, 0.59; 2,2-azonaphthalene 114.90, 91.12, 1.07; $p\text{-ClC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{OH}$ 211.56, 55.13, 2.74; $p\text{-HOC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{Cl}$ 189.2, 55.13, 2.54; $p\text{-HOC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{Cl}$ 153.93, 55.13, 2.18; $(\text{CH}_3)_2\text{C}(\text{CN})_2$ 330.93, 29.09, 3.81; $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{Et})_2$ 173.13, 51.69, 2.42; $(\text{CH}_3)_2\text{N}(\text{NH}_2)_2$ 143.49, 35.31, 2.33. The 1st compd. shows deviation from additivity of the dipole moment; this indicates the role of oxonium state for the O atom, whereas in the 2nd compd. the Ph group attracts an electron and yields a moment under an angle of 110° which reduces the observed moment. Vinyl ethers give results that are close to those of ordinary ethers. 2-Naphthalene derivs. show higher moments than do 1-analogs. The adipic acid derivs. show a slight dependence of moment on temp., as shown by detns. made at 50° (not cited however). G. M. K.

SYRKIN, Ya. K.

USSR/Chemistry Vitamins

Card : 1/1

Authors : Kazakova, V. M., Syrkin, Ya. K., and Shidlovskaya, A. N.

Title : Dipole moments of certain intermediate products from the synthesis of vitamin A (Brief report)

Periodical : Izv. AN SSSR, Otd. Khim. Nauk, 3, 562 - 563, May - June 1954

Abstract : The dipole moments of certain beta-ionone derivatives, which are intermediate products of vitamin A synthesis, were investigated and the dielectric constants in a phenol solution were determined at 25° by the heterodyne method. The results obtained are given in tables.

Institution : The M. V. Lomonosov Institute of Delicate Chemical Technology, Moscow

Submitted : February 16, 1954

SYRKIN, Ya. K.

USSR/Chemistry Refraction

Card : 1/1

Authors : Kikina, G. G., Syrkina, Ya. K., and Shott-L'vova, E. A.

Title : Refractions of molecules with conjugated bonds at different wave lengths

Periodical : Izv. AN SSSR, Otd. Khim. Nauk, 3, 563 - 564, May - June 1954

Abstract : The relation between refraction and additiveness is discussed and the problem of determining refraction extrapolated in accordance with infinitely long waves, is explained. The molecular refraction was measured for eight substances (benzene, naphthalin, anthracene, phenanthrene, acenaphthene, triphenylmethane, p-benzoquinone and phenanthrene quinones) using seven different wave lengths and the results are shown in table. One USSR reference.

Institution : The M. V. Lomonosov Institute of Delicate Chemical Technology, Moscow

Submitted : February 16, 1954

SYRIN, Ya. K.

5
(3)

9/ Dipole moments of some divinylacetylenic hydrocarbons.
A. N. Shidlovskaya, Ya. K. Syrin, and I. N. Naranov.
Doklady Akad. Nauk S.S.S.R. 94, 885-7 (1954).—The fol-
lowing dipole moments (in D.) were calcd. from dielec.
data of solns. of the hydrocarbons in C_6H_6 at 25°: divinyl-
acetylene 0.02, 5-methyl-1,5-hexadien-3-yne 0.51, 5-
methyl-1,5-heptadien-3-yne 0.61, 5-phenyl-1,5-heptadien-3-
yne 0.70, 4-(1-cyclohexen-1-yl)-1-buten-3-yne 0.80, 2,2-
dimethyl-4-(vinylethynyl)-3,4-dihydro-2H-pyran 1.20, and
vinylacetylene was 1.019, which might be ascribed to at.
polarization, in which case the moment of the compd. would
be zero. If the at. polarization of the other substances is
similar, the above values are 0.03–0.5 D. higher than real
values, but definitely above zero. The case of hydrogenation
corresponds to the magnitude of the dipole moment
found in this series. The phys. consts. of the substances
were: resp.: b_{11} 84°, n_D^{20} 1.5035, d_{20} 0.7850; b_{11} 29°, 1.4970,
0.7950; b_{11} 41°, 1.5030, 0.8020; b_{11} 94°, 1.5042, 0.9575;
 b_{11} 83°, 1.5480, 0.9135; b_{11} 93°, 1.5275, 0.9441; and b_{11}
53°, 1.4775, 0.8920.
G. M. Kosolapoff

MF
9-28-54

SYRKIN, YA. K.

USSR/ Chemistry - Conversion processes

Card 1/1 Pub. 22 - 26/47

Authors : Shnol', S. E.; Syrkin, Ya. K., Memb. Corresp., Acad. of Sc., USSR; Yakerson, V. I.; and Blyumenfeld, L. A.

Title : Conversions of alpha-naphthalinsulfonic acid into beta-naphthalinsulfonic acid

Periodical : Dok. AN SSSR 101/6, 1075 - 1078, Apr. 21, 1955

Abstract : The mechanism of conversion of alpha-naphthalinsulfonic acid into beta-naphthalinsulfonic acid was established by the marked atom method in combination with the paper chromatography and spectrophotometry methods. The absence of radioactivity in the calcium sulfate deposition used in liberating the radioactive sulfate, served as proof of perfect purity of the converted compound. The effect of temperature on the conversion process and the final results are discussed. One USSR reference (1944-1950). Table; diagram.

Institution : The M. V. Lomonosov Inst. of Prec. Chem. Techn., Moscow

Submitted : December 1, 1954

The temperature-independent paramagnetism of potassium
permanganate. Ya. K. Serkin and V. I. Belova.
Zh. fiz. khim. 47, 1927 (1973). — The
paramagnetic susceptibility of K₂MnO₄ was
measured at various temperatures. The results
showed that the paramagnetism is temperature-independent.

Syrkin, Ya. K.

the hydrogen exchange mechanism. Ya. K. Syrkin
London v. Inst. Pure Chem. T. 105

1.11
1951

SYRKIN, YA. K.

USER/Chemistry

Card 1/1 Pub. 40 - 22/25

Authors : Shott-L'vova, Ye. A., and Syrkina, Ya. K.

Title : Dipole moments of symmetrical trinitrobenzene derivatives

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 127-128, Jan 1956

Abstract : The dipole moments of trotyl, xylyl and styphnic acid were measured by the heterodyne method in a benzene solution at 25°. The effect of the nitro-group on the increase in the trotyl and xylyl values is explained. The necessity of considering atomic polarization in the cases investigated, is discussed. Five references: 1 USSR, 4 USA (1935-1953). Table.

Institution : Moscow Inst. of Fine Chem. Technol. im. M. V. Lomonosov

Submitted : November 1, 1955

Syrkin, Ya. K.

M.A. YOUTZ
2 copies

Dipole moments of allyl 2-dialkylaminovinyl ketones.
A. N. Shulovskaya, Ya. K. Syrkin, and N. K. Kochetkov
(M. V. Lomonosov Inst. Fine Chem. Technol., Moscow).
Izv. Akad. Nauk S.S.S.R., *Udal. Khim. Nauk* 1956,
254-6. --The following values of dipole moments (in D.)
were detd. at 25° in CCl₄ soln.: MeCOCH:CHNMe₂ 5.67;
MeCOCH:CHN(CH₃)₂ 5.23; MeCOCH:CHNMe 5.06;
PrCOCH:CHNMe₂ 4.83; iso-BuCOCH:CHNMe₂ 4.70;
the high polarity of the ketones is expected from their chem.
reactivity. G. M. Kosolapoff

Youtz

ADW
RM

SYRKIN, Ya.K.

Mechanism of hydrogen exchange. Ukr. khim. zhur. 22 no.1:23 '56.
(Hydrogen) (MIRA 9:6)

12

Dielectric polarization of compounds with hydrogen bonds
I. Complexes of proton-donor compounds with pyridine in
benzene as solvent. Lucjan Sobczyk and Jakub Jas. *Chem.*
(Inst. Precise Chem. Technol., Moscow). *Russ. Chem.*
30, 881-91 (1958) (Russian summary).—Dielec. polarization
(dipole moment, μ ; effective, P_{eff} , and additive, P_{add} ,
polarizations) was measured in binary systems formed by
 C_6H_5N (I) with $AcOH$ (II), $PrCOOH$ (III), $BzOH$ (IV),
 $CH_3CICOOH$ (V), CCl_3COOH (VI), picric acid (VII), $Ph-$
 CH (VIII), and trinitrofluorene (IX) in C_6H_6 as solvent. The
results are tabulated. The following values were found for
I-VII: 1-II, 2.93; I-III, 2.96; I-IV, 2.88; I-V, 4.67; I-VI, 7.78;
I-VII, 10.1. The polarity of the H bond exerted a clear effect
on acidity of proton-donor comp. VIII and IX did not show
proton-donor properties. Shattenshtein's theory (C.A. 49,
13746) on acids and bases was confirmed. II. Complexes
of organic acids with quinoline, acridine, and triethylamine.
Ibid. 883-9. —Effective (P_{eff}) and additive (P_{add}) polariza-
tions were measured in (acid-base-solvent)-type systems
formed by some org. acids with quinoline (I), acridine (II),
and triethylamine (III). ΔF was calculated as the difference
 $P_{add} - P_{eff}$. The results were tabulated. The dipole
moments were 1.98 and 0.63 D. for I and II. Increase of
conjugated double bonds in aromatic base rings caused the
increase of the dipole moments. The bond polarity can be
considered as the measure of acidity and basicity of org.
comps. in nonpolar solvent. III forms with org. acids the
strongest polar complexes. The forces existing in H bonds
are considered to some extent quantum-mech. in nature.
The properties of H bridge system are associated with the
valence levels of a proton-acceptor atom.

B.

POLAND/Physical Chemistry - Molecule. Chemical Bond

Abs Jour : Ref Zhur - Khimiya, No 9, 1958, 27665

Author : Sobczyk, L. and Syrkim, J.K.

Inst :

Title :

Dielectric Polarization of Systems Containing Hydrogen Bonds. II. Complexes of Organic Acids with Quinoline, Acridine, and Triethylamine.

Orig Pub : Roczniki Chem. 30, No 3, 893-899 (1956) (in Polish with a Russian summary)

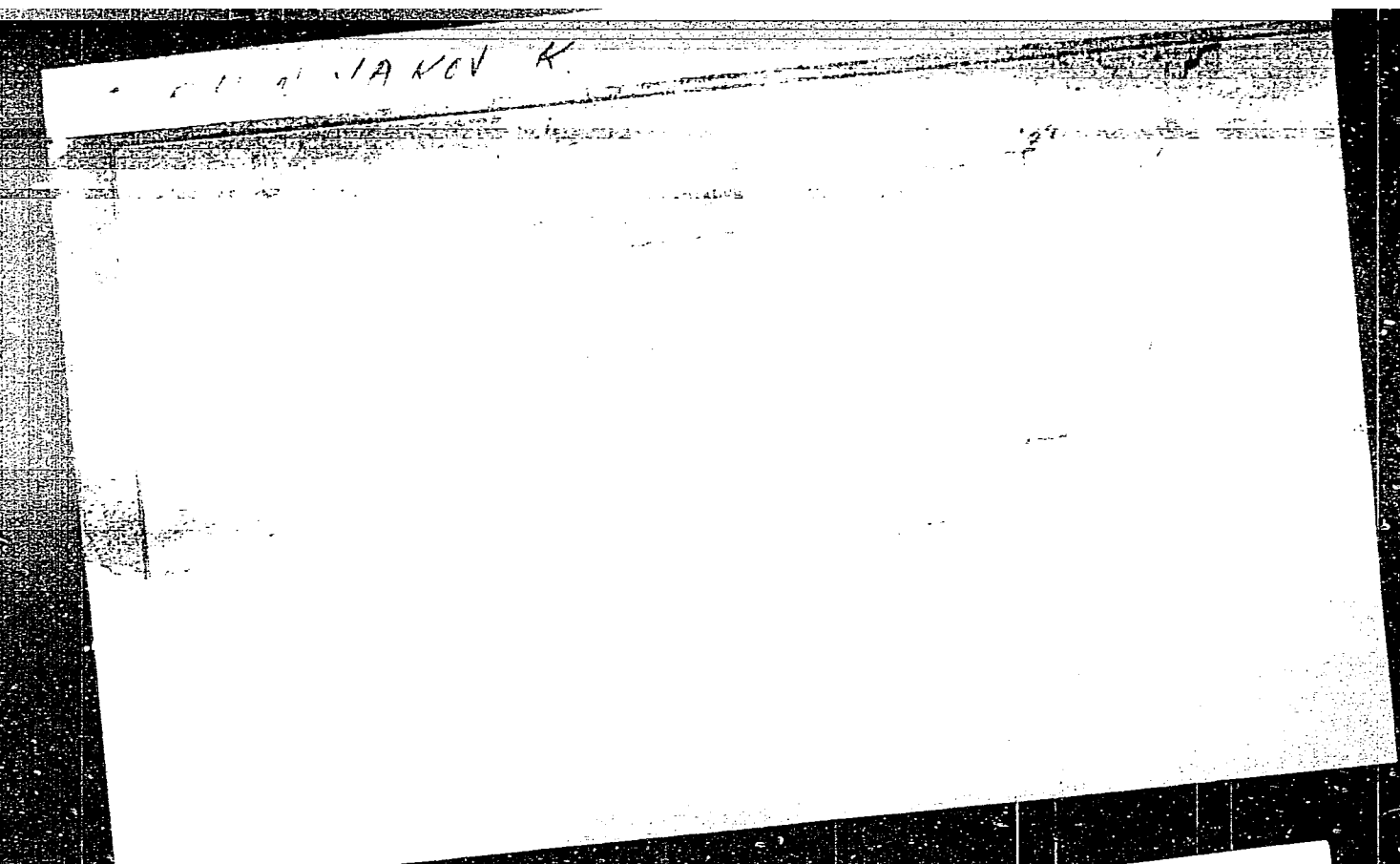
Abstract : The dielectric polarization of three-component systems (indifferent solvent, acid, and base) was measured. The effect of the properties of the base (dipole moment μ and ionization constant) and of the valence state of the proton acceptor on the polarization of the hydrogen bond $\Delta \mu$ is discussed. Complexes (K) formed by pyridine (I), quinoline (II), acridine (III), and triethylamine (IV) with propionic (V), chloroacetic (VI),

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3.

"APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R001654310008-3



APPROVED FOR RELEASE: 08/31/2001

CIA-RDP86-00513R001654310008-3"

AUTHORS
TITLE

PERIODICAL
ABSTRACT

Syrkin, Ya. K.

Moiseyev, I.I., Syrkin, Ya.K., Corresponding Member, AN USSR
The Mechanism Underlying the Hydration of Olefines in the Water
Solutions of Strong Acids.
(O mekhanizme gidratatsii olefinov v vodnykh rastvorakh sil'nykh
kislot - Russian).
Doklady Akademii Nauk, 1957, Vol 115, Nr 3, pp 541-544 (U.S.S.R.)

The hydration of butylene, triptane, trimethylethylene, and methyl-
cyclobutane in 1-5 M HNO_3 solutions is subject to an equation of
first order. Between the observed velocity constant of the reaction
 k and the acidity function $\text{Of Hammett } H$ there is a dependence
 $p-H_o = \lg k + \text{const.}$ (1), the coefficient p being $1(0.98 \pm 1.11)$. The
satisfying of this equation served as basis for the (here given) hy-
dration mechanism of the olefines. The thermal effect of the first
stage is composed of the following processes: a) proton desolvation
-260, b) proton connection to the olefine under formation of a π -
complex Q_x , c) "solvation" of the formed π -complex Q_x , d) dissol-
ving of the water molecule + 10 cal bound to the proton. For the
calculation of Q_x within the scale of the resonance integral of
cannot be deciphered), the knowledge of the resonance integral of
the δ -binding between the atoms C and H in the π -complex is neces-
sary. The δ -value can be estimated by means of a measure analogous
to that of Simonetta and Winstein. Approximative calculations of
the energy yield in the proton connection to the double binding
under the π -complex formation on the basis of various methods give
values of from 20 to 39 kcal. Thus the thermal effect of the first

Card 1/3

20-3-33/59

The Mechanism Underlying the Hydration of Olefines in the Water Solutions of Strong Acids.

not clear (Gelbshtein, Shcheglova and Temkin in the case of decomposition of formic acid). It is obvious that the character of kinetic dependence is maintained independently of the fact whether the solvation of proton transfer to the complex of reacting molecules precedes, or viceversa. According to the equations for the reaction velocity coefficients which a part of the equations for the reaction velocity constant, either the equation (I) or (II): $k'_0 = k'_0(H_2O^+)$ or eventually the intermediate dependences can be satisfied. On the strength of the dependences (I) and (II) it can only be said for the general case that the transition complex contains a molecule of the basis and a proton. Nothing can, however, be said regarding the existence of other particles. The less it is possible to determine with what part of the complex the proton is connected; There are 7 Slavic references.

ASSOCIATION Moscow Institute for Fine Chemical Technology "M.V. Lomonosov".
(Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M.V. Lomonosova).
SUBMITTED January 28, 1957
AVAILABLE Library of Congress.
Card 3/3

SYRKIN, Ya. K.

SHOTT-L'VOVA, Ye.A.; SYRKIN, Ya.K.; LEVKOYEV, I.I.; SYTNIK, Z.P.

Dipole moments of some rhodanine merocyanine dyes, derivative.
Dokl. AN SSSR 116 no.5:804-807 0 '57. (MIRA 11:2)

1.Chlen-korrespondent AN SSSR (for Syrkin). 2.Moskovskiy institut
tonkoy khimicheskoy tekhnologii im. M.V. Lomonosova i Vsesoyuznyy
nauchno-issledovatel'skiy kino-foto-institut.
(Rhodanine) (Dipole moments)

Syrkin, Ya. K.

62-2-22/28

AUTHORS: Shidlovskaya, A. N., Syrkin, Ya. K.,
Nazarov, I. N., Sokolov, D. V.,

TITLE: The Dipole Moments of the Steric Isomers of 2-Methyl-4-Keto-Decahydroquinolines (Dipol'nyye momenty prostranstvennykh izomerov 2-metil-4-ketodekagidrokhinolinov)

PERIODICAL: Izvestiya AN SSSR Otdeleniya Khimicheskikh Nauk, 1958, Nr 2, pp. 241-241 (USSR)

ABSTRACT: The authors measured the dipole moments of the above-mentioned isomers which were synthesized by Sokolov. Dielectric polarizations were determined according to the heterodyne method in benzene solutions (at 25°C). The results of this work are given in table 1. Formulae, melting temperatures as well as an information on the investigated concentrations, the full polarizations, P_{∞} , orientation polarizations P_{or} and so on are also given in the table. The congruence of the moments of all isomers indicates the similar configurations of the polar groups (table 1). There is 1 table.

~~Card 1/2~~ Inst. Fine Chem. Technology in M.V. Lomonosov

SOV/62-58-6-3/37

AUTHORS: Kazakova, V. M., Syркин, Ya. K.

TITLE: The Dielectric Polarization of Molecular Iodine- and Bromine Compounds (Dielektricheskaya polyarizatsiya molekulyarnykh soyedineniy yoda i broma)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 6, pp. 673 - 678 (USSR)

ABSTRACT: An explanation was found for the abnormal properties of "brown-violet" and "brown" iodine solutions (in C_6H_6 , C_5H_5N), viz.: increased solubility of iodine, its reactivity, etc. in connection with the investigation of ultraviolet absorption spectra (possibility of the presence of iodine complexes with molecules of the solvent in the solution). Data concerning the interaction between bromine and organic substances are rarely found in published works. In the course of the present paper the authors give a report about measurements carried out of the dielectric polarization of 22 ternary systems of iodine and bromine (acceptors) with various organic compounds (donors) in benzene as a solvent. In some cases stable molecular compounds (with high polarity) were found to be formed at the expense of the

Card 1/2

SOV/62-58-12-17/22

5(2)
 AUTHORS: Syrkin, Ya. K., Belova, V. I.
 TITLE: Magnetic Susceptibility and Structure of Nitrosyl Complexes of Ruthenium (Magnitnaya vospriimchivost' i stroyeniye nitrozil'-nykh kompleksov ruteniya)
 PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 12, pp 1492-1493 (USSR)
 ABSTRACT: In this paper the authors give a brief report mentioning that the magnetic susceptibility of 4 nitrosyl compounds was measured. All compounds turned out to be diamagnetic. The results of the measurements are mentioned in the table. It seems probable that the nitrogen electrons $2s^2 2p^3$ take part in the bonds of nitrogen with oxygen and the ruthenium atom. The data in publications concerning other diamagnetic nitrosyl complexes of ruthenium (Ref 2), agree with this concept. The authors thank V. N. Filimonova and N. A. Parpiyev for the compound samples supplied by them. There are 1 table and 5 references, 2 of which are Soviet.

~~Card 1/2~~ Incl. Gen. & Inorganic Chem. in N. S. Kurnakov

SOV/78-3-9-5/38

AUTHORS: Belova, V. I., Syrkina, Ya. K.

TITLE: The Magnetic Susceptibility of the Complex Compounds of Osmium
(Magnitnaya vospriimchivost' kompleksnykh soyedineniy osmiya)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1958, Vol 3, Nr 9, pp 2016-2023
(USSR)

ABSTRACT: The magnetic susceptibility of osmium compounds of different valence was investigated. The investigations were carried out at 77 and 300° K. The methods of preparing the initial compounds are described. The non-magnetic compounds of osmium belong to the type of the covalent complexes. Also the osmium compounds with two nuclei are non-magnets. An unusual magnetism is ascertained in tetravalent osmium compounds of the type K_2OsCl_6 . A comparison of the ligand field theory and Pauli's theory shows that Pauli's theory provides more satisfactory results in compounds with covalent bindings and the ligand field theory in compounds without covalent binding. The hexamine and pentamine of osmium are paramagnetic. At room temperature the hexamines have a magnetic moment of $1,77\mu_B$ and at 77° K one of $1,65\mu_B$. For the pentamines the magnetic moment at room

Card 1/2

SOV/78-3-9-5/38

The Magnetic Susceptibility of the Complex Compounds of Osmium

temperature is $1,7\mu_B$, and at $77^\circ K$ it is $1,5\mu_B$. Osmium dioxide has crystal lattices of the rutile type and is non-magnetic. OsS_2 at room temperature is diamagnetic and at $77^\circ K$ paramagnetic. The unusual magnetic properties of some osmium complex compounds are explained by the ligand field theory. There are 2 tables and 8 references, 2 of which are Soviet.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii imeni N. S. Kurnakova, Akademii nauk SSSR (Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, AS. USSR)

SUBMITTED: February 1, 1958

Card 2/2

SYRKIN, Ya. K.

SOV/A-27-6-4/6

AUTHORS:

Syrkin, Ya. K., Moiseyev, I. I. (Moscow)

TITLE:

The Mechanisms of Organic Reactions (Mekhanizmy organicheskikh reaktsiy) Hydrolysis and Esterification (gidroliz i esterifikatsiya)

PERIODICAL:

Uspekhi khimii, 1958, Vol. 27, No. 6, pp. 717 - 736 (USSR)

ABSTRACT:

Esterification and hydrolysis are two parts of one and the same equilibrium. Therefore conclusions drawn with respect to the mechanism of one of these reactions refer also to the mechanism of the other. The character of the hydrolysis and of the kinetic laws governing the reaction depend on the structure of the ester (which was subjected to hydrolysis) on the one hand, and on the medium and on the catalyst on the other. This indicates the possibility of the existence of various different mechanisms. A. K. E. Day (Day) and C. K. Ingold (Ingold) are cited who attempted systematically to explain the experimental material (hydrolysis of esters by elementary processes). The various limiting stages are then enumerated. The energy of four of the total of eight of these

Card 1/3

SOV/14-27-6-4,6

The Mechanisms of Organic Reactions.
Hydrolysis and Esterification

stages, (which are referred to here as A¹, A², A³, and A⁴) is discussed. Also the papers by C. W. Kinshelwood (Kinshelwood) and his collaborators (Refs 2, 10) are mentioned and discussed. Mention is also made of the articles by R. S. Eydler (Eydler) and S. A. Landskroener (Landskroener) (Ref 19): "Investigation of the Influence Exercised by the Solvent on the Hydrolysis of the Ethyl Acetate, Methyl Propionate, Acetamide, Propionamide, and Acrylamides of Various Acids in Alkaline and Acid Media". Next, also other pertinent transitional situations in hydrolysis reactions are discussed. Mention is made also of the method of nuclear-magnetic resonance (Ref 22) as well as of facts connected with the influence exercised by substituents in the benzene ring upon the kinetics of the hydrolysis of benzoate ester (Refs 31, 32), as also of Ingold's terminology (Ref 1): Attempt at explaining the rent observed on the alkyl-oxygen bond. Summary: The material discussed in this article shows that the hypotheses concerning unstable intermediate ions are as yet not sufficiently well founded and must in most cases be revised. Besides, the part played by cyclical active complexes in the reactions of hydrolysis has hitherto been underestimated. It is, however, certain that

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30474-27-6-4/6

The Mechanisms of Organic Reactions.
Hydrolysis and Esterification

these complexes play an important part in the reactions of hydrolysis. It must further be considered that in a number of cases it is possible that the reaction may develop by way of acyclic, open, and active complexes without the participation of carbon ions. There are 1 table and 61 references, 4 of which are Soviet.

1. Organic materials--Chemical reactions
2. Esters--Hydrolysis
3. Chemical reactions--Analysis

Card 3/3

AUTHORS:

Syrkin, Ya.K., Moiseyev, I.I. (Moscow)

SOV/74-27-11-3/5

TITLE:

Mechanism of Organic Reactions (Mekhanizmy organicheskikh reaktsiy)
Diene Synthesis (Diyenovyy sintez)

PERIODICAL:

Uspekhi khimii, 1958, Vol 27, Nr 11, pp 1321-1336 (USSR)

ABSTRACT:

In this paper various hypotheses on the course of the diene synthesis are investigated. Two courses were assumed:

1) Formation of a transition complex with open side-chain (biradical), or biradical and subsequent cyclization.

2) Formation of a cyclic transition complex.
Computations of the activation energies necessary in any case have proved that the intermediate formation of a biradical and the subsequent cyclization are energetically impossible (attempt of dimerization of butadiene and formation of cyclohexane from butadiene and acetylene. The activation energy of the formation of cyclohexane is higher than that of the dimerization of butadiene) (Table 1). Experiments carried out by Eisler and Wassermann (Ref 3) confirmed the assumption of the cyclic transition complex. For the formation of a 6-cycle of two butadiene molecules the cis-form of diene is necessary which is possible only at the

Card 1/2

Mechanism of Organic Reactions. Diene Synthesis;

SOV/74-27-11-3/5

free mobility of 6 electrons in the cyclic transition complex with little expenditure of energy, however, not in the biradical. In the meeting of cyclic dienes and dienophils spatial configurations are formed. Also in this case two possibilities exist. Formation of an endo- and an exo-configuration. Mainly endo-configuration is formed. Hitherto it has not been known why preference is given to endo-configuration. There exist several assumptions in this connection, however, each of them may only explain one fact, others are in contradiction to them. Woodward assumes the formation of an inter-molecular donor-acceptor binding (Ref 32) between the participants in diene synthesis (ionic linkage). Hudson and Robinson (Refs 36,37) assume the formation of a hybrid ion. Finally the authors arrived at the result that the double bonds play the most important part in the active complex. In the general case of diene synthesis it was therefore found that it takes place over a 6-cyclic active complex. Alder had expressed this fact in a similar way: for the reaction of the diene synthesis the presence of a hydrogen atom at a carbon atom with double bond is necessary and this double bond must be able to migrate. There are 3 tables and 54 references, 9 of which are Soviet..

Card 2/2

AUTHORS: Shidlovskaya, A. N., Syrkin, Ya. K., Corresponding 20-118-5-33/59
Member of the AS USSR, Nazarov, I. N., Member of
the AS USSR, (Deceased), Kucherov, V. F.

TITLE: Dipole Moments of Ethers of the Isomeric Cyclohexane-1,2-Di-
carboxylic Acids (Dipol'nyye momenty efirov .zomernykh
tsiklogeksan-1,2-dikarbonovykh kislot)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 5, pp. 967-969
(USSR)

ABSTRACT: Usually it is proceeded from the fact that the fauteuil-like
configuration with a maximum number of equatorial substituents
is the most stable. This assumption was chiefly confirmed by
the investigation of different cyclic compounds which have
methyl and hydroxyl groups as substituents. In this context
the investigation of such compounds is interesting which
have more strongly polar substituents (references 1,2). In
the series of the 1,2-substituted cyclohexanes 3 isomers are
possible: a cis-isomer with an equatorial-axial position of
the substituents ($\text{H} - \text{a}$), or a trans-isomer in a diequatorial
form ($\text{a} - \text{a}$) or in a diaxial form ($\text{a} - \text{a}$). Dipole moments of

Card 1/4

Dipole Moments of Ethers of the Isomeric Cyclohexane-1,2-Di- 20-118-5-33/59
carboxylic Acids

maleic acid is greater than of that of fumaric acid. This is moreover confirmed by the cis-configuration of the compound number 3 (table 1). Table 2 shows moments of molecules which differ from those treated above by having an additional methyl group at C₄. As could be expected for the isomers 1 and 2 equal values of the moments were obtained, as the moment of the CH₃-group is equal to that of the C-H group.

The isomers 3 and 4 have somewhat greater moments. Isomer 4 is also the most stable. All other isomers are finally transformed into isomer 4. Contradictory to the formula (references 4-6) the authors maintain that for substituents of the type of ethers of the cyclohexane-1,2-dicarboxylic acids which contain irregular groups the moment of the diaxial isomer (a-a) may not be set equal to zero. In order to determine the configuration of the isomers of the dimethylethers of cyclohexane-1,2-dicarboxylic acid the dipole moments were computed by assuming a free rotation of the COOCH₃ groups, taking into consideration their direction as irregular groups in relation to the cyclohexane nucleus. The moment of the isomer a-a was determined as 2,30 D. The experimental value of the moment

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APPROVED FOR RELEASE: 08/31/2001 20-118-5-33/59
CIA-RDP86-00513R001654310008-3"
Dipole Moments of Ethers of the Isomeric Cyclohexane-1,2-Di-
carboxylic Acids

of the cis-isomer lies between the computed values 2,51 - 2,30 D. The experimental moment of the trans-isomer (=2,14) does not correspond to the computed value of the moment of the isomer a-a if a free rotation is assumed. There are 2 tables and 9 references, 2 of which are Soviet.

ASSOCIATION:

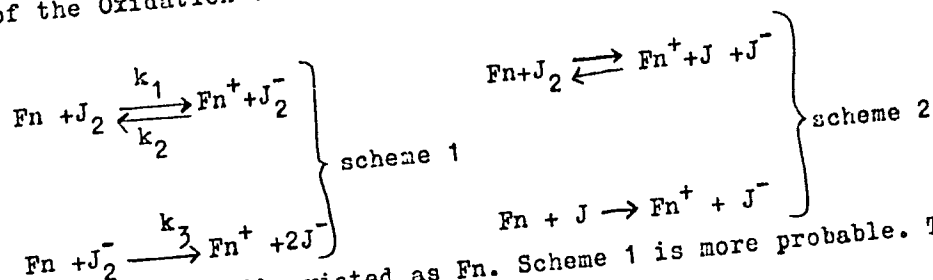
Moskovskiy institut tonkoy khimicheskoy tekhnologii im.
M. V. Lomonosova (Moscow Institute for Refined Chemical
Technology imeni M. V. Lomonosov)

SUBMITTED:

October 1, 1957

Card 4/4

The Kinetics of the Oxidation of Ferrocene by Iodine SOV/20-120-1-32/63



Ferrocene is abbreviated as Fn. Scheme 1 is more probable. The authors give the expression

$$\frac{d[\text{Fn}^+]}{dt} = \frac{2k_1k_3[\text{Fn}]^2[\text{J}_2]}{k_2[\text{Fn}^+] + k_3[\text{Fn}]}$$

for the velocity of oxidation, which then is specialized by simplification. Perhaps the reaction takes place with a previous formation of a molecular compound FnJ_2 in which the ferrocene occurs as donor of an electron. The authors studied the oxidation of ferrocene by iodine in 93- and 96% alcohol. In the case of an iodine excess the equilibrium of the reaction $\text{Fn} + 3/2 \text{J}_2 \rightleftharpoons \text{Fn}^+ + \text{J}_3^-$ is dislocated to the side of the production of ions. The velocity of the existing

Card 2/4

The Kinetics of the Oxidation of Ferrocene by Iodine SOV/20-120-1-32/63

experimental conditions is low for which reason it can be neglected in the investigation of the kinetics of the oxidation. The course of the change of the concentration of the ferrocenium ions is in every experiment described by the equation

$$d[Fn^+]/dt = k([Fn]_0 - [Fn^+])^2, \text{ where } k \text{ denotes a constant quantity. The kinetic data do not contradict the condition of the intermediate formation of an instable radical ion } J_2^-.$$

The activation energy and the factor before the exponent for the conversion of the electron from the ferrocene to the iodine are determined graphically from the temperature dependence of the velocity of reaction. The experiment supplied the following data: for the activation energy 14,6 kcal.mol⁻¹ and for the factor before the exponent the value 9.10¹¹ l.mol⁻¹ sec⁻¹. There are 2 tables and 9 references.

ASSOCIATION: Institut tonkoy khimicheskoy tekhnologii im.M.V.Lomonosova
(Institute of Fine Chemical Technology imeni M.V.Lomonosov)

Card 3/4

SOV/20-121-6-28/45
Corresponding Member,
Academy of Sciences, USSR, Levkoyev, I. I., Deychmeyster, M. V.

AUTHORS: Shott-L'vova, Ye. A., Syrkin, Ya. K.,
Academy of Sciences, USSR, Levkoyev, I. I., Deychmeyster, M. V.

TITLE: The Dipole Moments of the Hemioxanines of the Derivatives of
3-Ethylrhodanine and Indandione (1,3) (Dipol'nyye momenty
gemioksaninov proizvodnykh 3-etilrodanina i indandiona (1,3))

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 121, Nr 6, pp 1048-1051
(USSR)

ABSTRACT: The authors measured (at 25°) the dipole moments of some hemi-
oxanines containing 3-ethylrhodanine groups and indandione
groups by the heterodyne method in benzene. A table gives the
formulae, the upper and the lower limiting values of the measur-
ed concentrations, the total polarization, the electron polari-
zation, the values of the dipole moments in Debye (Debye)
units, and the position of the maximum of absorption of the
solutions of some pigments in alcohol (λ_{\max}). According to
experimental results, compounds which differ only by the length
of the polymethine group, have very different moments. An increase
of the number of the double bonds between polar groups

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SOV/20-121-6-28/45

The Dipole Moments of the Hemioxanines of the Derivatives of 3-Ethylrhodanine and Indandione(1,3)

$(>C=O \text{ and } -\overset{\text{R}}{\underset{\text{R}_1}{\text{N}}})$ always causes an increase of the moment.

Various results are then given and discussed. Although the moment of indandione (1,3) 2,72 D is greater than that of 3-ethyl-rhodanine (1,75 D), the moments of the monomethine-hemioxanines have a noticeably lower value for the derivatives of indandione (1,3). This is probably, caused by the different directions of the moments in 3-ethylrhodanine and indandione. The variations of the investigated absorption spectra of the hemioxanines, which are caused by an elongation of their polymethine chain, agree with the conclusions concerning the structure of these compounds which were drawn from the investigation of their dipole moments. There are 1 table and 13 references, 5 of which are Soviet.

SUBMITTED: May 9, 1958

Card 2/2

5(4), 15(6)
AUTHORS:

SOV/20-122-1-27/44
Kartsev, G. N., ~~Syrkin~~, Ya. K., Corresponding Member,
Academy of Sciences, USSR, Mironov, V. F., Chernyshev, Ye.A.

TITLE:

The Dipole Moments of Some Silicon-Organic Compounds
(Dipol'nyye momenty nekotorykh kremniyorganicheskikh soedineniy)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 1, pp 99-102
(USSR)

ABSTRACT:

The authors measured the dipole moments of some silicon-organic compounds according to the heterodyne method at 25° in benzene. The extrapolated polarizations were calculated according to a formula of Gedestrand. For compounds which contain silicon, the atomic polarization has to be taken into account. The experimental results are given in a table. A distinctive peculiarity of the silicon compounds is the increased polarity with respect to the corresponding carbon bonds. According to the available data, the bond moment of Si-H may be estimated to 1D, and the bond moment of Si-C - to 0,6D. In both of these cases, the positive end of the dipole is directed towards the silicon. In the bonds

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The Dipole Moments of Some Silicon-Organic Compounds SOV/20-122-1-27/44

Si-O and Si-halogen, the weight of the ionic state is higher. Numerous and detailed data are given. There are 1 table and 5 references.

ASSOCIATION: Moskovskiy Institut tonkoy khimicheskoy tekhnologii im.
M. V. Lomonosova
(Moscow Institute of Fine Chemical Technology imeni M. V.
Lomonosov)

SUBMITTED: May 15, 1958

Card 2/2

5(4)

AUTHORS: Dyatkina, M. Ye., Syrkin, Ya. K., SOV/20-122-5-25/58
Corresponding Member, Academy of Sciences, USSR

TITLE: The Three-Center Orbits and the Structure of Cyclo-
propane and Other Compounds With Three-Member Rings
(Trekhtsentryye orbity i stroyeniye tsiklopropana i
drugikh soyedineniy s trekhchlennymi kol'tsami)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 5,
pp 837 - 839 (USSR)

ABSTRACT: According to the results obtained by various previous
papers (Refs 1,2,3) the formation of three-center
orbits is not a special case and occurs rather frequently
in the case of various molecules. Such orbits may,
according to the authors' opinion, exist in a far
greater number of cases than hitherto assumed. By
utilizing the ideas concerning three-center orbits
it is possible to explain the structure of various
molecules. This is the case especially with a number
of compounds with an insufficient number of electrons,

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The Three-Center Orbits and the Structure of Cyclopropane and Other Compounds With Three-Member Rings

SOV/20-122-5-25/56

which are formed by the attachment of a proton to the valence-saturated molecules. For H_2^+ only the hypothesis of the existence of three-center orbits is of use. The author believes that something similar applies also to CH_3^+ . Three-center orbits are probably possible also in C_3 molecules with three-member cycles. It is just this special configuration of a three-member ring with angles of 60° that is indicative of a possible realization of three-center orbits also in this case. The authors then dwell somewhat more in detail upon this hypothesis, which is suited not only for cyclopropane but also for various of its analogues. (e.g. ethylene oxide and ethylenimine). It may also be possible that three-center orbits form the basis of $Fe_3(CO)_9$. There are 3 figures and 8 references, 3 of which are Soviet.

SUBMITTED:

July 7, 1958

Card 2, 2

SYRKIN, Ya. K.

"Fundamental Problems of the Theory of Chemical Bonds."

report presented at the Plenary Session, 8th Mendeleyev Congress, Moscow, 14-18
Mar 1959.

5(4), 5(3)
AUTHOR:

Syrkin, Ya. K.

SOV/62-59-2-8/40

TITLE:

Six-Membered Cyclic Active Complexes in Organic Chemistry
(Shestichlennyye tsiklicheskiye aktivnyye kompleksey v
organicheskoy khimii)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 2, pp 238-246 (USSR)

ABSTRACT:

In order to clarify the mechanism of a large part of the molecular organic reactions in this paper 6-membered cyclic active complexes were investigated. Molecular and ionic reactions can proceed over cyclic active complexes in which breaking and forming bonds alternate. The method of molecular orbits permits in its simplest form already important conclusions with respect to the 5-, 6-, and 7-membered cycles. Theory shows in all cases the occurrence of 3 conjugating orbits. It is assumed that 5-, 6-, and 7-membered cycles with 6 electrons play an important role also in chemical kinetics. Presumably, the conclusions drawn from calculations of the energies of π -electrons with respect to the energies of these cycles can be qualitatively transmitted to cycles with σ -bonds. From this point of view previously

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Six-Membered Cyclic Active Complexes in Organic
Chemistry

SOV/62-59-2-8/40

(Ref 2) the hydrogen exchange between alcohols and heavy water had been investigated. The experiments showed (Ref 3) that the reaction proceeds rapidly at normal temperature in solutions and vapors. This seems to exclude both the radical and the ionic mechanism. The very rapid exchange between water and alcohols was also proved by means of nuclear paramagnetic resonance (Ref 4). The method of tagged atoms abolished the earlier conception that the reactions proceed in several stages. It was proved that they occur in one process. The rearrangements with a displacement of groups from the 1-position, passing the meta-position, into the ortho-(with inversion) or para-position (without conversion) are a very convincing counter-evidence against the radical mechanism. On comparison of the reactions investigated which are either exothermal or thermoneutral, certain conclusions had been drawn as to the activation energies. Under certain conditions the formation of 4-membered cycles is possible as it is the case on the decomposition of octafluoro cyclobutane C_4F_8 . This decomposition proceeds monomolecularly at low pressure in a certain temperature range

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Six-Membered Cyclic Active Complexes in Organic
Chemistry

SOV/62-59-2-8/40

complexes by reacting and regenerating in one process. In this connection the mechanisms which postulate the participation of unstable intermediary ions (carbonium ions and carbanions) were subjected to a criticism since they were in most cases neither proved nor energetically confirmed. The mechanisms suggested with cyclic complexes correspond to the data on the isotopic exchange. There are 1 table and 20 references, 3 of which are Soviet.

ASSOCIATION: Institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova
(Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: June 11, 1957

Card 4/4

SOV/62-59-3-3/37

5(4)

AUTHOR:

Syrkin, Ya. K.

TITLE:

Five- and Seven-membered Cyclic Activated Complexes in Organic Chemistry (Pyati- i semichlennyye tsiklicheskiye aktivnyye komplekсы v organicheskoy khimii)

PERIODICAL:

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 389 - 400 (USSR)

ABSTRACT:

In the present paper 5- and 7-membered cyclic activated complexes were suggested for a number of organic reactions. The class of the 5-membered complexes comprises all cases in which 6 electrons move in the field of 5 centers. One of the cycle members gives 2 electrons: It is either the negative ion of the OH^- , OC_2H_5^- , halogentype or an atom with an undivided pair of electrons which takes part in the activated complex. During the reaction the division of the pair of electrons takes place. Hereby a bond is formed between the one electron and its cycle partner. The other electron is transferred into the electrophilic atom which is transformed by it into a negative ion. 5-membered cyclic

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Five- and Seven-membered Cyclic Activated Complexes in SOV/62-59-3-3/37
Organic Chemistry

activated complexes with less than 6 electrons can also be formed. It is important only that there are not more than 6 electrons in such a cycle. Less than 6 electrons are no hindrance but an advantage, because in this case occupation starts from lower orbits. It might therefore be expected that the occurrence of a 5th center which represents an empty orbit will considerably reduce the activation energy when 4 electrons are present. In the case of 7 centers there are likewise 3 combining levels for 6 electrons. There the role of the center consists in representing a free (empty) orbit. The 7th center can be a catalyst of the BF_3 type. The processes proceeding according to a 7-membered cycle probably include the isomerization of butane into isobutane in the presence of AlCl_3 . The pinacol rearrangement takes place in the presence of boron oxide, aluminum oxide, and strong acids. It can be produced in the form of a 7-membered activated complex in which the catalyst is probably the 7th center. In all cases investigated the 6 electrons move within the cycle field. It

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Five- and Seven-membered Cyclic Activated Complexes in SOV/62-59-3-3/37
Organic Chemistry

must be emphasized that 6 electrons in the field of 7 centers have a certain resemblance with a deficiency structure. Reactions are possible in which the electron transfer is the principal part. The kinetics of the electron transfer which was determined according to the extension of the nuclear resonance line, e.g. between the tetramethyl p-phenylene diamine and Wurster's blue as well as between other substances (Ref 15), is distinguished by high velocities. Sometimes an electron transfer takes place by means of a catalyst. There are 16 references, 2 of which are Soviet.

ASSOCIATION: Institut tonkoy khimicheskoy tekhnologii im. M.V.Lomonosova
(Institute of Fine Chemical Technology imeni M.V.Lomonosov)

SUBMITTED: June 15, 1957

Card 3/3

5(4)

AUTHOR:

Syrkin, Ya. K.

SOV/62-59-3-4/37

TITLE:

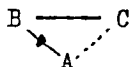
Mechanism of Molecular Rearrangements, Hydrolysis, Esterification, and Aldehyde Reactions in the Light of the Theory of Cyclic Active Complexes (Mekhanizmy molekulyarnykh peregruppirovok, gidroliza, eterifikatsii i reaktsiy al'degidov v svete teorii tsiklicheskikh aktivnykh kompleksov)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 401-411 (USSR)

ABSTRACT:

In the present paper the mechanisms of some molecular rearrangements, hydrolysis, esterification, and aldehyde reactions were investigated. A specific peculiarity of a number of rearrangements is the transition of the system A-B-C to the system B-C-A. The explanation of this process by the migration of the free radical or ion frequently seems to be arbitrary. In numerous cases the intermolecular proceeding of the rearrangement was proved. As component the arrangement



enters into the active complex, in which the BC

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bond is maintained, the AB bond breaks and AC is formed.

Mechanism of Molecular Rearrangements, Hydrolysis, SOV/62-59-3-4/37
Esterification, and Aldehyde Reactions in the Light of the Theory of Cyclic
Active Complexes

The group A covers a wide range during the reaction. The occurrence of half bonds B....A and A....C is possible if the 6-membered active complex is formed without considerable expenditure of energy. A general conclusion from a number of papers is that the rearrangement into ortho-position takes place with inversion and into para-position without inversion. The reaction is intermolecular (and monomolecular). The process is obviously neither radical nor ionic. In the case of rearrangement into para-position the transition stage might be the process in ortho-position. It may be assumed that the process takes place through a 6-membered complex. For hydrolysis and esterification the fact is important that in many cases a rupture of the acyl-oxygen bond takes place. This was proved by means of methods of the tagged atoms and optical activity. Furthermore in most of the esters the alkali hydrolysis proceeds as a second-order reaction. This is in accord with two different mechanisms. In the reactions investigated in which H_3O^+ and OH^- participated there is a

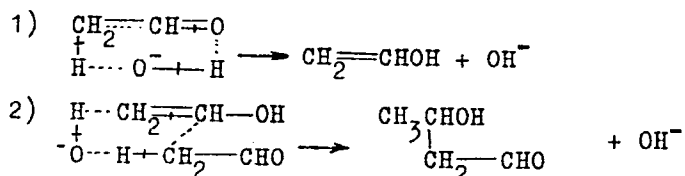
Card 2, 5

Mechanism of Molecular Rearrangements, Hydrolysis, SOV/52-59-3-4/37
Esterification, and Aldehyde Reactions in the Light of the Theory of Cyclic
Active Complexes

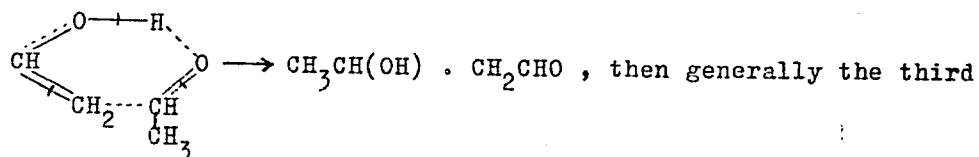
common characteristic, namely the active complex in which breaking and nascent bonds alternate, is formed more readily if the charges alternate (in ions or polar bonds). This additional electrostatic effect reduces the energy of repulsion and favors the formation of active cyclic complexes. The investigation of reactions of acid anhydrides with amines by means of tagged O^{18} proved that the carbonyl oxygen of the amide was the carbonyl oxygen of the anhydride. This reaction may easily be produced by a 4- or 6-membered complex. For the reaction of Cannizzaro it was proved by means of the isotopic method that the oxygen is directly transferred from one aldehyde molecule to the other. According to conditions and reagents the reaction proceeds in some cases according to a third-order equation and in other cases to a fourth-order equation. This suggests the possibility of different mechanisms. The third-order reactions fit well into the structure of a 6-membered complex. For the fourth-order the following mechanism is suggested:

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Mechanism of Molecular Rearrangements, Hydrolysis, SOV/62-59-3-4/37
Esterification, and Aldehyde Reactions in the Light of the Theory of Cyclic
Active Complexes



If the second stage proceeds according to



order results. Consequently this is the competition of two active complexes. In both cases instead of $\text{CC}\pi$ the $\text{C}-\text{C}\sigma$ bond is formed in consequence of the reaction. This is, so to speak, the thermodynamic justification of the reaction. In the case of the fourth order in the active complex in the presence of the reacting and regenerating OH^- -ion a favorable

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Mechanism of Molecular Rearrangements, Hydrolysis, SOV/62-59-3-4/37
Esterification, and Aldehyde Reactions in the Light of the Theory of Cyclic
Active Complexes

succession of the charges takes place. The reactions between aromatic aldehydes and aliphatic ketones in the presence of bases may be explained by 6-membered active complexes. There are 11 references, 1 of which is Soviet.

ASSOCIATION: Institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova
(Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: June 21, 1957

Card 5/5

SyRKIN, YAK.

AUTHORS: Ruz'minskiy, A.S. and Bass, S.I.
 TITLE: The VIIIth Mandeleev Congress (VIII Mandeleevskiy
 s'ezd)

90W/138-59-4-14/4

PERIODICAL: Kanchuk i Rezhina, 1959, Nr 4, pp 47-48 (USSR)
 ABSTRACT:

This Congress on Pure and Applied Chemistry was held from 16th to 22nd March, 1959 in Moscow, and was attended by 1 500 representatives of Soviet research institutes, chemical factories and many foreign associations. Academician A.N. Nesmeyanov opened the meeting and emphasised the importance of the Mandeleev Congresses. V.S. Fedorov, representative of the Gosudarstvennyy Komitet Sovetskaya Ministroy SSSR, Po Khimii (State Committee of the Council of Ministers of the USSR for Chemistry) drew attention to Soviet achievements in chemistry. The following papers were read during the Congress: V.A. Syrkina on the "Basic Problems in the Chemistry of Polymers"; A.N. Nesmeyanov on "The Periodic Law" of D.I. Mendeleev and Organic Chemistry"; N.M. Semenov

Card 1/2

on "Basic Problems of Chemical Kinetics"; A.P. Alekseyev on "Chemical Aspects of Utilizing Atomic Energy"; M.K. Bychkov, Corresponding Member of the Academy of Sciences of the USSR, on "The Basic Problems of the Theory of Chemical Bonds" etc. Special attention was drawn to the chemistry of high-molecular compounds and to methods for preparing starting materials for the synthesis of polymers by starting materials for the modification of the properties of petroleum crudes, further graft polymers, radiation and initiation etc.). V.A. Syrkina discussed three main aspects of polymer chemistry: preparation of polymers which could be used within wide temperature ranges; preparation of polymers and easily accessible polymer materials and processing of polymers. Further details of the lectures are to be published at a later date.

Card 2/2

5(4)

AUTHOR:

Syrkin, Ya. K.

SOV/62-59-4-6/42

TITLE:

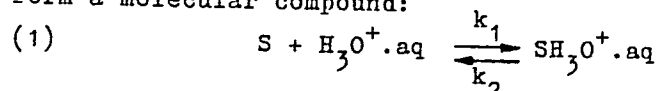
Mechanism of Molecular and Acid-base Catalytic Reactions in Organic Chemistry (Mekhanizmy molekulyarnykh i kislotnoosnovnykh kataliticheskikh reaktsiy v organicheskoy khimii)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 600-610 (USSR)

ABSTRACT:

In the present work it has been attempted to investigate a number of reactions without use of free radicals, carboxyl ions and carbon anions. As contrasted with existing conceptions the author believes that an addition of the ion, e.g., of $H_3O^+_{aq}$, takes place in the first stage of the acid-basic catalysis to form a molecular compound:

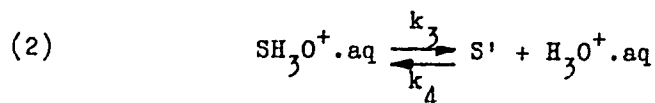


In the second stage the reaction proceeds from the molecular compound (substrate with molecule or ion) via an active cyclic complex with a succession of breaking and originating bonds:

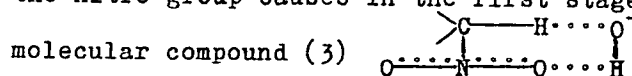
Card 1/3

SOV/62-59-4-6/42

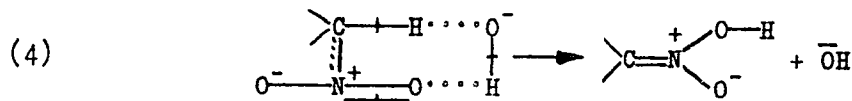
Mechanism of Molecular and Acid-base Catalytic Reactions in Organic Chemistry



Depending on the value of the specific rates k_1 , k_2 , k_3 , k_4 the kinetic equation may have one form or the other, under participation of the concentrations and activities. The reaction may, but need not depend on the acidity function. Based on these conceptions the action of the OH^- ion on the nitroparaffins which contain hydrogen in addition to the carbon connected to the nitro group causes in the first stage the formation of the



As a result of the reaction via the active six-member complex this compound is transformed into (4):



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This method of active cyclic complexes has been used in some re-

SOV/62-59-4-6/42

Mechanism of Molecular and Acid-base Catalytic Reactions in Organic Chemistry

actions of Friedel-Crafts, Würtz, Ziegler, Grignard, Kizhner, Knevenagel', in some cases of decarboxylation, and nitration, and in the reactions of organic peroxides. Some mechanisms which have been investigated may be subject to discussion and are possibly more complicated. It is believed, however, that numerous organic molecular reactions will be found which correspond to the formulated course of reaction via active five-, six-, and seven-member complexes upon closer consideration. This problem requires further theoretical and practical investigation. There are 25 references, 2 of which are Soviet.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: June 24, 1957

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5(4),24(3)

AUTHORS:

Kazakova, V. M., Syrkin, Ya. K.

SOV/62-59-4-38/42

TITLE:

Paramagnetic Electron Resonance of Metal Ketyls (Elektronnyy paramagnitnyy rezonans metallketilov)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 755-756 (USSR)

ABSTRACT:

This is a short communication on the investigation of the spectra of the paramagnetic electron resonance of 6 ketyls obtained by the effect of metallic potassium or sodium on respective ketones, among them of hexamethyl acetone sodium-ketyl by Nazarov. The reactions were carried out in carefully purified ether or benzene in a dry nitrogen current at room temperature. Ketyls were obtained in the form of colored solid precipitates on pieces of metal. The measurements were carried out at a frequency of 9,800 megacycles on a radiofrequency spectrometer with magnetic field modulation. The width of the absorption bands $\Delta H_{1/2}$ of the ketyls was measured in comparison to the standard substance - powderized 1,1-diphenylpicryl-hydracyl. The results are shown in the table. The factors of

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Paramagnetic Electron Resonance of Metal Ketyls

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the spectroscopic splitting were similar for all ketyls and approached the g -factor of hydracyl: $g_{\text{ketyl}} - g_{\text{hydracyl}} \pm 0.0010$. There are 1 table and 6 references, 1 of which is Soviet.

ASSOCIATION: Institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova
(Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: September 16, 1958

Card 2/2

5(4)

AUTHORS: Dyatkina, M. Ye., Syrkin, Ya. K.

SOV/78-4-6-12/44

TITLE: On the Problem of the Stereochemistry of the Bimolecular Substitution in Complex Compounds (K voprosu o stereokhimii bimolekulyarnogo zameshcheniya v kompleksnykh soyedineniyakh)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 6, pp 1285-1290 (USSR)

ABSTRACT: The stereochemistry of the bimolecular substitutions in octahedral and quadratic complexes was investigated. It was found that in the case of the transition of the configuration of the complex from the quadratic to the bipyramidal one a substitution of the addends occurs as well as a change of the valence state of the central atom. In the case of the bimolecular substitution in octahedral complexes it is possible that the free orbits with greater principal quantum number take part in the development for the production of complex compounds with additional substitution groups. The intermediate complexes with tetragonal pyramidal structure are important in the kinetics of the reaction of the bi- and tetravalent platinum. In the case of the substitution in complexes with quadratic configuration the formation reaction proceeds under

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SOV/78-4-6-12/44

On the Problem of the Stereochemistry of the Bimolecular Substitution in Complex Compounds

formation of intermediate complex compounds with tetragonal and pyramidal configuration. There are 7 figures and 6 references, 3 of which are Soviet.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii im. N. S. Kurnakova
Akademii nauk SSSR
(Institute of General and Inorganic Chemistry imeni N. S. Kurnakov of the Academy of Sciences, USSR)

SUBMITTED: March 25, 1958

Card 2/2

Syrkin, Ya. K.

5(2)

AUTHOR:

Zvyagintsev, O. Ye.

BOV/78-4-9-43/44

TITLE:

The 6th Mendeleev Congress on General and Applied Chemistry

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 9, pp 2178-2182 (USSR)

ABSTRACT:

The Congress mentioned in the title was held in Moscow from March 16 to 23, 1959. More than 4000 delegates and guests from 19 countries participated. It was opened by the President of the Organizational Committee, Academician A. N. Nesmeyanov, who asked the participants to discuss the development of chemistry and chemical technology in the USSR in the light of the decisions of the 21st Congress of the CPSU. The following members read papers in the plenary sessions: V. S. Fedorov, Chairman of the Gosudarstvenny komitet sovetskikh ministrov (State Committee on Chemistry of the Council of Ministers, USSR); Tasks of Scientific and Technical Progress in the Chemical Industry; Y. A. Kargin: Basic Problems of Polymer Chemistry; A. N. Nesmeyanov: The Periodic System and Organic Chemistry; V. S. Fedorov: Basic Problems of Chemical Kinetics; V. I. Spitsyn: The Present State of D. I. Mendeleev's Periodic Law; A. P. Vinogradov: Basic Problems of Radiochemistry; V. A. Engel'gardt: Basic Problems of Biochemistry; A. V. Sokolov: Chemical Problems of Agriculture in the USSR; V. S. Nikolayev: Main Tasks of the Construction of Chemical Machinery and Apparatus; Ye. K. Syrtin: Basic Problems of the Theory of Chemical Linkages; and A. P. Aleksandrov: Chemical Prospects for the Use of Atomic Energy. An appeal to all chemists of the USSR was drawn up in fulfillment of the great tasks posed by the 21st Congress of the CPSU.

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SOV/78-4-11-46/50

5(2)

AUTHORS:

Moiseyev, I. I., Fedorovskaya, E. A., Syrkin, Ya. K.

TITLE:

New Complexes of Palladium With Unsaturated Organic Ligands

PERIODICAL:

Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 11,
pp 2641-2642 (USSR)

ABSTRACT:

Palladium chloride reacts with allyl alcohols in acidified aqueous solution to form the compound C_3H_5PdCl . At temperatures between 15 and 20°, a yellow α -form develops which is stable up to 130°; at temperatures below 10°, the green β -form develops which already decomposes at 50°, dissolved in benzene even at 25°. The α -form is assumed to be identical with the compound $Pd_2Cl_2 \cdot C_6H_{10}$ as described in reference 1. Both forms are diamagnetic. The allyl group seems to be capable of forming a special type of complex compounds which is also proved by the reaction of palladium chloride with mesityl oxide. A diamagnetic yellow substance $PdClC_6H_9O$ develops which is stable up to 176°. Its infrared spectrum is discussed, and assumptions on the kind

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New Complexes of Palladium With Unsaturated Organic
Ligands

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of the bond with PdCl are made. A detailed report on further investigations in this field will follow. The authors thank V. I. Belova for the measurements of magnetic susceptibility, I. Yu. Kokoreva for the measurements of the dipole moments, and Yu. G. Borod'ko for recording the infrared spectra. There is 1 reference.

SUBMITTED: July 9, 1959

Card 2/2

SOV/74-28-8-1/6

5(0)

AUTHOR:

Syrkin, Ya. K.

TITLE:

The Present Stage of the Problem of Valence
(Sovremennoye sostoyaniye problemy valentnosti)

PERIODICAL:

Uspekhi khimii, 1959, Vol 28, Nr 8, pp 903-920 (USSR)

ABSTRACT:

In this article, the author discusses the problem of valence. The modern theory of the chemical bond is based upon data on the properties of individual molecules. These include especially their physical properties, furthermore their chemical behavior, which shows the reactivity of the molecules, as well as experimental data on the chemical reaction mechanism. A generalization of all these experimental data is represented by the quantum-mechanical theory of the chemical bond. A quantum-mechanical analysis shows that the presence of two electrons with opposite spin in the field of two nuclei is, as far as energy is concerned, more favorable than the presence of each electron in the field of its own nucleus. The development of a chemical bond is, therefore, accompanied by a considerable diminution of free energy of the system. Also the ideas of a covalent or unipolar bond is based hereupon. Since the establishment of the theory of the covalent bond a great number

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The Present Stage of the Problem of Valence

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of new data have been added, which demands an extension of the theory. Experiments show that besides the above-mentioned type of a covalent bond donor-acceptor bonds also are of great importance. They are formed at the expense of an electron pair of the one atom - the donor - and the free orbit of the other atom - the acceptor. The special feature of donor-acceptor bonds is the fact that they raise the number of interatomic valence bonds by using a great number of electrons and empty orbits. On the basis of donor-acceptor bonds a higher coordination is obtained. In comparison with the theory of covalent bonds by Geytler-London the idea of donor-acceptor bonds offers nothing new in principle. They only differ by the question as to from where the electrons are added (one electron from each atom or one pair from one atom, and the free orbit from the other). From the data available it resulted that the representation of two-center bonds cannot explain the structure of numerous molecules. The method of molecular orbits seems to be more appropriate. Originally it resulted from the observation of conjugated bonds in inorganic chemistry in which it has widely been employed. This method is a generalization of all

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The Present Stage of the Problem of Valence

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kinds of bonds, ranging from ionic to covalent bonds, all these bonds are therein combined in a uniform theory. In the author's opinion, the method of molecular orbits is especially applicable actual to inorganic complex compounds. Though it has been employed only for a short time, the first investigations in this field have already proved promising. Quantum-mechanical ideas and particularly the method of molecular orbits obviously will give a far more exact and complete explanation of chemical bonds than all previous theories. Even if this theory gives, for the time being, an explanation rather than a prediction, there exist still a number of predictions, particularly for conjugated bond systems. At the present stage of chemistry the leading role belongs to the experiment. Nevertheless it would be a great mistake to underrate the value of the theory. Mendeleyev (Ref 31) has this already recognized. There are 3 figures and 31 references, 7 of which are Soviet.

ASSOCIATION: Moskovskiy in-t tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

Card 3/3

SOV/79-29-1-40/74

AUTHORS: Syrkin, Ya. K., Yakerson, V. I., Shnol', S. E.

TITLE: The Transformation Mechanism of the o-Toluenesulfonic Acid Into the p-Toluenesulfonic Acid (Mekhanizm prevrashcheniya o-toluolsul'fokisloty v p-toluolsul'fokisloty)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 1, pp 187-194 (USSR)

ABSTRACT: Previously (Ref 1) the authors tried to clear the question of the migration mechanism of the sulfo group on the transformation of α -naphthalene sulfo acid into the β -isomer. Although it was proved that an intramolecular rearrangement takes place, some points remained unsolved. Hollemann and Calland (Ref 2) investigated the transformation of o-toluenesulfonic acid into the para-isomer. The authors assume that the process proceeds intramolecularly and not, as supposed, by way of the hydrolysis and subsequent sulfurization in the para-position. They proved that there is no desulfurization because the rearrangement prevails. Furthermore, the sulfurization yields 4% meta-product which previously had not been found. Ye. A. Shilov and F. M. Vaynshteyn (Ref 3) investigated the transition of the ortho-isomer into the para-isomer by means of radioactive S^{35} at

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The Transformation Mechanism of the o-Toluenesulfonic Acid Into the p-Toluenesulfonic Acid

120 and 126°; they concluded that the reaction takes place intermolecularly. They underline, however, that they had not been able to determine the specific radioactivity of the rearrangement products in the initial stage of the reaction. In order to investigate this process more exactly the authors thought it useful to pay special attention to the transformation from the very beginning of the reaction. They did not only apply the radioactive but also the spectroscopic method. In the present paper they tried to connect the radiochromatographic method with the spectrophotometric one. It was found that in acid medium the process mainly proceeds intramolecularly; in part, however, through the medium, i. e. intermolecularly. For the explanation of the intra-and intermolecular reaction process a scheme is suggested. There are 4 figures and 10 references, 4 of which are Soviet.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii (Moscow Institute of Fine Chemical Technology)

SUBMITTED: December 17, 1957
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SOV/79-29-2-70/71

AUTHORS: Belova, V. I., Vol'pin, M. Ye., Syrkin, Ya. K.

TITLE: Letter to the Editor (Pis'mo v redaktsiyu)
The Magnetic Receptivity of Tropyli Salts (Magnitnaya vospriimchivost' soley tropiliya)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 693-694 (USSR)

ABSTRACT: The compound C_7H_7 is known to be stable in the cyclic structure form of the positively charged $C_7H_7^+$ ion. It is of interest to determine the diamagnetic receptivity of this ion and to compare it with the receptivity of other cyclic molecules, e.g. benzene and cyclooctatetraene. For this purpose the following compounds were synthesized and their receptivity was determined: tropyli hexachloro platinate $(C_7H_7)_2PtCl_6$, tropyli perchlorate $C_7H_7ClO_4$ and tropyli mercury tetraiodide $(C_7H_7)_2HgJ_4$. A report on the synthesis of the first two compounds had already been made earlier (Ref 2). Tropyli mercury tetraiodide was first synthesized as follows: aqueous $HgCl_2$ -solution and

Card 1/3 KJ were added to C_7H_7Br solved in water (2.34 g, 3.72 g, and 9.1 g,

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Letter to the Editor. The Magnetic Receptivity of Tropyl Salts

respectively). $(C_7H_7)_2HgJ_4$ was separated and filtered, washed with 10 % KJ solution of water and alcohol and finally recrystallized from nitromethane. The magnetic receptivity was determined according to Saxsmith (Saksmit) at room temperature and with certain strength values of the magnetic field (Table 1). Unlike other platينات, the receptivity values of tropyl chloro platinate differ from one another in various syntheses. The table shows therefore the highest determination of receptivity, which surely corresponds to the purest sample (from the magnetic point of view). The value of magnetic receptivity in the organic cations of tropyl $C_7H_7^+$ was calculated from experimental data. The anion value of receptivity is given in the fourth column of the table. The receptivity value of ion $PtCl_6^{2-}$ was determined according to reference 3, that of the ion HgJ_4^{2-} according to reference 4. The value of ion ClO_4^- was obtained from table 3 (from the book by Selwood, P.W.) (Ref 5). The value of receptivity of ion $C_7H_7^+$, from various tropyl compounds, is recorded in the last column of the table. Pascal's additive scheme concerning the receptivity values of the compounds, containing conjugate bonds

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Letter to the Editor. The Magnetic Receptivity of Tropyli Salts

(C_6H_6 , $C_7H_7^+$, C_8H_8) is judged negatively by the authors and their own explanations are given.- There are 1 table and 6 references, 2 of which are Soviet.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii i Institut elemento-organicheskikh soyedineniy Akademii nauk SSSR (Institute for General and Inorganic Chemistry and Institute for Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: July 20, 1958

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5(0)

SOV/30-59-6-2/40

AUTHORS: Syrkin, Ya. K., Corresponding Member, Academy of Sciences, USSR,
Dyatkina, M. Ye., Doctor of Chemical Sciences

TITLE: The Present State of Quantum Chemistry (Sovremennoye
sostoyaniye kvantovoy khimii)

PERIODICAL: Vestnik Akademii nauk SSSR, 1959²⁹ Nr 6, pp 13-25 (USSR)

ABSTRACT: The beginnings of quantum chemistry are to be found in the work by W. Heisenberg (1926) who investigated the first multi-electron system - the helium atom - as well as in the work by Heitler and London who used the same method for investigating the hydrogen molecule H_2 (1927). In these investigations the physical reasons for the formation of a covalent bond were discovered for the first time, however, no accurate solution of the Schrödinger equation for these problems could be obtained. For this reason an approximation method had to be applied. It may be seen from it that in the near future it will hardly be possible to obtain reliable values in quantum chemistry of the dissociation energy by theoretical computations. Concerning the problems of a survey of the existing approximated and exact

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The Present State of Quantum Chemistry

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methods of computation the authors of this article refer to the paper by P. Levdin (footnote 1). Furthermore, a number of interesting results obtained in the field of qualitative conclusions from chemical quantum computations are demonstrated, the values of which are acknowledged by the authors. The concepts concerning the directivity of valencies is regarded as a success of qualitative quantum chemistry. Chemical quantum computations of covalent atomic radii in condensed aromatic hydrocarbons also proved to be successful. The problem of the application of quantum-chemical methods for determining spectral properties of chemical compounds is also of interest. There are 1 figure and 1 reference. ✓

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PHASE I BOOK EXHIBITION NOV/1921

Akademika nauk SSSR. Institut fizicheskoy khimii

Problemy khimicheskoy kataliza. (t. 10: Fizika i fiziko-khimiya kataliza. Problemy khimicheskoy kataliza. (vol. 10: Physics and Physical Chemistry of Catalysis) Moscow, Izd-vo AN SSSR, 1960. 461 p. Errata slip inserted. 2,600 copies printed.

Eds.: S.Z. Roginskii, Corresponding Member of the Academy of Sciences USSR, and O.Y. Erylov, Candidate of Chemistry; Ed. of Publishing House: A.L. Bakhvutsa; Tech. Ed.: G.A. Astaf'yeva.

PURPOSE: This collection of articles is addressed to physicists and chemists and to the community of scientists in general interested in recent research on the physics and physical chemistry of catalysis.

CONTENTS: The articles in this collection were read at the conference on the Physics and Physical Chemistry of Catalysis organized by the Odessa Khimicheskii nauk AN SSSR (Section of Chemical Sciences, Academy of Sciences USSR) and by the Academic Council on the problem of "the scientific bases for the selection of catalysts." The Conference was held at the Institut fizicheskoy khimii AN SSSR (Institute of Physical Chemistry of the AN USSR) in Moscow, March 20-23, 1958. Of the great volume of material presented at the conference, only papers not published elsewhere were included in this collection.

III. SOME GENERAL PRINCIPLES OF CATALYSIS

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5.3610

78084

SOV/62-60-1-30/37

AUTHORS: Shott-L'vova, Ye. A., Syrkin, Ya. K.

TITLE: Dipole Moments of Dicyclohexylammonium Nitrite. Brief Communications

PERIODICAL: Izvestiya akademii nauk SSSR, otdeleniye khimicheskikh nauk, 1960, Nr 1, pp 139-140 (USSR)

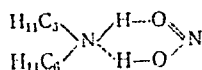
ABSTRACT: Dipole moment for dicyclohexylammonium nitrite (I), or dicyclohexylamine nitrite as the authors called it, was determined in a benzene solution at 25°. Dielectric constants of 0.000109, 0.000094, and 0.0000809 mole solution of I were found. They are 2.2738, 2.2733, and 2.2729, respectively. The electronic polarization of I is 65.4 cm³. According to the literature data, α is equal to 11.17, 10.75, and 10.35; β is 0.8. The dipole moment for I, calculated according to the above data is equal to 4.14, 0.04 x 10⁻¹⁸. Since the dipole moment obtained is too low for a salt, the authors conclude I in a nonpolar

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Dipole Moments of Dicyclohexylammonium
Nitrite. Brief Communications

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solvent, does not exist in a salt form $[(C_6H_{11})_2 NH_2^+]$
 $[NO_2]^-$. The data obtained indicate HNO_2 and dicyclo-
hexylamine in a nonpolar solvent can form a molar
compound with two hydrogen bonds:



The authors express their gratitude to M. N. Polteva
for supplying material for measurement.

ASSOCIATION: M. V. Lomonosov Institute of Fine Chemicals Technology
(Institut tonkoy khimicheskoy tekhnologii imeni
M. V. Lomonosova)

SUBMITTED: June 19, 1959
Card 2/2

SYRKIN, Ya.K.

Oxane compounds of oxygen. Zhur. strukt. khim. 1 no.3:389-390
S-O '60. (MIRA 14:1)

1, Moskovskiy institut tonkoy khimicheskoy tekhnologii imeni M.V.
Lomonosova.
(Oxygen compounds) (Oxane)

KARTSEV, G.N.; SYHKIN, Ya.K.; MIRONOV, V.F.

Dipole moments of some germanium organic compounds. Izv. AN
SSSR Otd.khim.nauk no.5:948-949 My '60. (MIRA 13:6)

1. Institut tonkoy khimicheskoy tekhnologii imeni M.V.
Lomonosova.
(Germanium organic compounds--Dipole moments)

SYRKIN, Ya.K.

Types of active complexes and their role in homogeneous catalysis.
Probl. kin. i kat. 10:225-239 '60. (MIRA 14:5)
(Catalysis) (Complex compounds)

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S/062/60/000/012/018/020
B013/B054

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AUTHORS: Savitskiy, A. V. and Syrkin, Ya. K.
TITLE: Equilibrium Reactions of Ferrocene and Ruthenocene
Oxidation With Iodine
PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, 1960, No. 12, pp. 2254-2256

TEXT: The authors briefly report on a study of the absorption spectra of ternary $\text{Fc-I}_2\text{-C}_6\text{H}_6$ and $\text{Rc-I}_2\text{-C}_6\text{H}_6$ systems, which was conducted to determine the thermodynamic characteristics (ΔF , ΔH , ΔS) of ferrocene (Ref. 1) and ruthenocene oxidation with iodine. The following designations are used: Fc is $(\text{C}_5\text{H}_5)_2\text{Fe}$; Rc is $(\text{C}_5\text{H}_5)_2\text{Ru}$; Mc is dicyclopentadienyl metal $(\text{C}_5\text{H}_5)_2\text{Me}$. Iodine sublimated in the usual way, and ruthenocene and ferrocene purified by sublimation in vacuo, were used in the experiments. The measurements were made on apparatus of the types C Φ 4 (SF4) and C Φ 2M (SF2M) at different temperatures in a glass bulb ($d=4.33$ cm) kept at

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Equilibrium Reactions of Ferrocene and
Ruthenocene Oxidation With Iodine

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constant temperature. The two apparatus gave agreeing results. The $\text{Fc}-\text{I}_2-\text{C}_6\text{H}_6$ system was investigated in Ref. 4. This paper studied the deviation of the optical density D from the addition value D_0 at different wavelengths (Fig. 1). The same figure gives the absorption spectrum of $(\text{CH}_3)_3\text{C}_6\text{H}_5\text{NI}_3$ as a calibration measure for the optical density of the triiodide ion. The experiments revealed the existence of a linear dependence $(D - D_0) [\text{Fc}]_0^{-1} [\text{I}_2]_0^{-3/2} = a + b[\text{I}_2]_0$ (Fig. 2). a and b are empirical constants. A similar dependence was observed in the system $\text{Ru}-\text{I}_2-\text{C}_6\text{H}_6$ (Fig. 3). A comparison of these dependences with the absorption spectra of $(\text{CH}_3)_3\text{C}_6\text{H}_5\text{NI}_3$ and $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{NI}_5$ (Fig. 4) confirmed the assumption concerning the origin of FcI_3 and FcI_5 . The equilibrium constants were found from the corresponding constants a and b at different temperatures. The values of the equilibrium constants K_1 and K_2 are given in Table 1, the values of ΔF , ΔH , and ΔS in Table 2. The different oxidation rate of ferrocene and ruthenocene observed can be explained by the

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Equilibrium Reactions of Ferrocene and
Ruthenocene Oxidation With Iodine

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fact that the activation energies are determined by the quantity ΔH of the electron transfer. The calculation shows that the electron transfer is weakly endothermic, and that ΔH in the case of ruthenocene is by $1.5 \text{ kcal.mole}^{-1}$ smaller than in the case of ferrocene. On the basis of data given in Table 2, the value of ΔH can be determined for the reaction $\text{Rc} + \text{FeI}_3 = \text{RcI}_3 + \text{Fc}$ in benzene. In this case, it is $1.5 \text{ kcal . mole}^{-1}$.

Ruthenocene is thermodynamically stabler than ferrocene. The bond of the metal with the ring, which is more solid in ruthenocene, is confirmed by the study of infrared spectra of the two compounds (Ref. 8). On the basis of these data, and the similar values of ionization potentials, it may be concluded that the ruthenicinium cation is thermodynamically stabler than the ferricinium cation. There are 4 figures, 2 tables, and 8 references, 1 Soviet, 4 US, 2 British, and 1 German. X

ASSOCIATION: Institut tonkoy khimicheskoy tekhnologii im.M.V. Lomonosova
(Institute of Fine Chemical Technology imeni M.V.Lomonosov)

SUBMITTED: May 25, 1960

Card 3/3

SYRKIN, Ya.K.

Formation of three-center bonds in chemisorption. Zhur. struk.
khim. 1 no.2:189-199 JI-Ag '60. (MIRA 13:9)
(Adsorption) (Chemical bonds)

S/078/60/005/008/019/031/XX
B023/B066

AUTHORS: Dyatkina, M. Ye., Syrkin, Ya. K.

TITLE: Participation of d-Orbits in the Bonding of Atoms With a-
and p-Electrons

PERIODICAL: Zhurnal neorganicheskoy khimii, 1960, Vol. 5, No. 8,
pp. 1663-1668

TEXT: The authors studied the increased stability of single bonds between equal atoms. These bonds constitute the simpler type of covalent bonds if they are not complicated by a partially ionic character. But even these bonds may have anomalies. Even in cases where atoms forming diatomic molecules have only one unpaired electron, there is a number of deviations from the simple distribution of energy in single bonds. All data confirm the low stability of single bonds in alkali metals, oxygen, nitrogen, and fluorine, and also increased stability of such bonds in elements of the copper sub-group, in phosphorus, sulfur, chlorine, and their analogs. The increased stability of single bonds between equal atoms of sulfur, phosphorus, chlorine, and their analogs, as well as of elements of the copper sub-group

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Participation of d-Orbits in the Bonding
of Atoms With a- and p-Electrons

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as compared with oxygen, nitrogen, fluorine, and alkali metals may be explained by the participation of electron pairs and free d-orbits in bonding. Electron pairs and free d-orbits may also take part in the intermolecular interaction in crystals and metallic compounds. Investigations of the authors are not mentioned. There are 6 references: 2 Soviet, 1 Belgian, 1 German, and 2 US. ✓

ASSOCIATION: Institut obshchey i neorganicheskoy khimii im. N. S. Kurnakova Akademii nauk SSSR (Institute of General and Inorganic Chemistry imeni N. S. Kurnakov of the Academy of Sciences USSR)

SUBMITTED: April 24, 1959

Card 2/2

BOROD'KO, Yu.G.; SYRKIN, Ya.K.

Raman scattering line intensities of CCl_4 , SiCl_4 , and GeCl_4 mixed
with benzene, p-xylene, and cyclohexane. Opt. i spektr. 9 no.5:
677-679 N '60. (MIRA 13:11)

(Carbon tetrachloride--Spectra)

(Silicon chloride--Spectra)

(Germanium chloride--Spectra)

SIRKIN, I.K. [Syrkin, Ya.K.]

Present state of the problem of valence. Analele chimie 15 no.1:3-23
Ja/Mr '60. (EEAI 9:8)
(Valence (Theoretical chemistry))

~~66223~~ 69633S/074/60/029/04/01/005
B008/B014

5.3200

AUTHORS: Syrkin, Ya. K., Moiseyev, I. I.TITLE: Mechanisms of Some Reactions With the Participation of Peroxides //

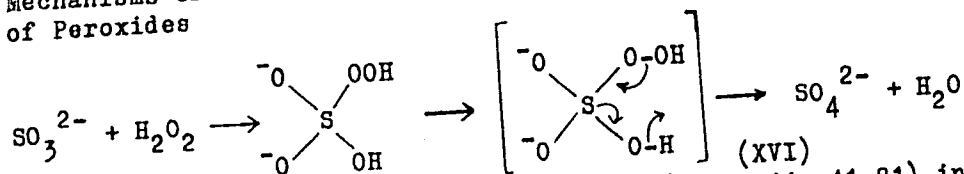
PERIODICAL: Uspekhi khimii, 1960, Vol. 29, No. 4, pp. 425-469

TEXT: In the article under review, the authors describe their attempts to study a great number of reactions. They endeavored to find the mechanisms which correspond to the experiment or at least do not contradict it. They intended above all to clarify the role played by cyclic, activated complexes in reactions of peroxide compounds. First, they studied the oxidation of ketones and aldehydes with per acids and hydrogen peroxide (Refs. 1-40). It was found that the reaction is nearly always a second-order reaction, and is catalyzed by acids. The mechanisms under consideration had one feature in common, i.e., the formation of intermediates by addition of the hydrogen peroxide to the carbonyl bond. It seems to be reasonable to assume that several oxidation reactions of inorganic compounds also proceed via corresponding addition products. The authors established that the following scheme underlies the oxidation mechanism:

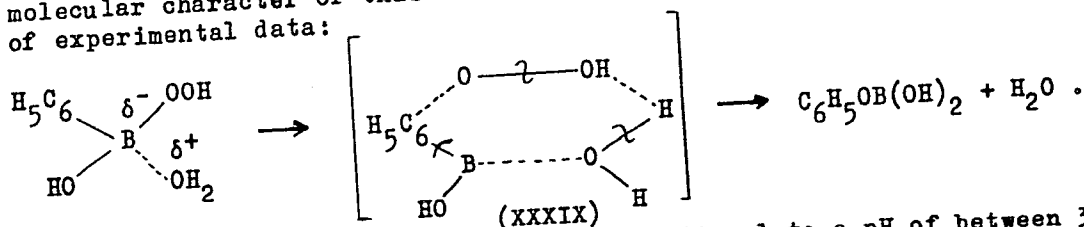
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Mechanisms of Some Reactions With the Participation of Peroxides

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B008/B014



The rearrangement of 9-decalylperbenzoate (Refs. 11, 41-81) indicated the intramolecular character of this reaction. The following scheme was set up on the basis of experimental data:



The elevation of the reaction rate is proportional to a pH of between 3 and 6. The corresponding acid and hydrogen peroxide are formed during the hydrolysis of a per acid (Refs 24, 70, 82). This reaction is accompanied by disruption of the acyl-oxygen bond. The reaction rate is proportional to the concentration of hydrogen ions, but not to the acidity of the solution. The mechanism previously suggested for several hydrolytic reactions of organic esters makes it possible to explain

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Mechanisms of Some Reactions With the Participation of Peroxides

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experimental data (p. 442). The corresponding hydroperoxides are formed during the reaction of hydrogen peroxide with alcohols (Refs. 41, 84-92). Also this reaction is accompanied by disruption of the alkyl-oxygen bond. The polarity of this bond is of great importance to the course of reaction. Presumably, the cyclic mechanism and mechanisms in which carbonium ions are formed compete with one another in this process. The thermal decomposition of per acids, esters of per acids, and acyl peroxides (Refs 49, 93-122) is accompanied by total or partial separation of CO_2 according to molecular mechanisms without free radicals participating in this reaction. It is often very difficult, sometimes even impossible, to distinguish the molecular reaction from the reaction of the radicals in the cage of the solvent. A few data obtained by means of optically active acyl-peroxides are indicative of a simultaneous occurrence of molecular and radical processes. In some cases, it is also possible that the individual processes compete with one another. The first stage of the decomposition reaction is presumably the decomposition of the molecule to form acyl-oxy radicals, as is the case with the noninitiated decomposition of benzoyl peroxide. The recombination of the radicals immediately after their formation is termed "primary recombination". In explaining the cage effect the authors refer to a paper by one of the authors mentioned in Ref. 125. This effect, which might be important to the mechanisms of several reactions in solutions, possibly consists in an interaction between two radicals or molecular fragments being in the cage, i.e., when they are surrounded by the

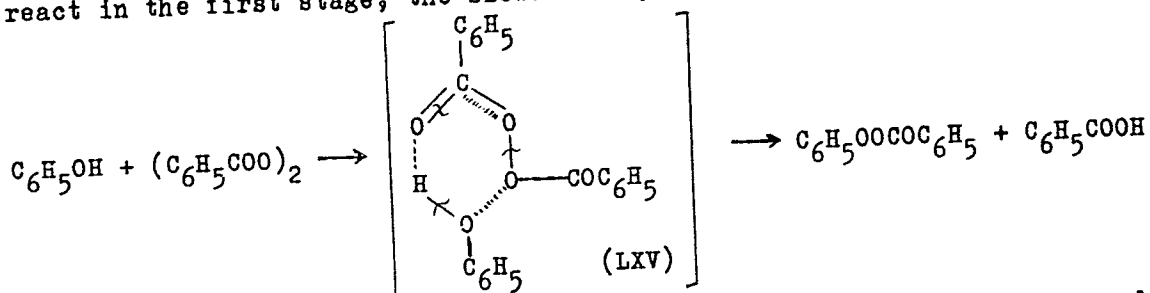
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Mechanisms of Some Reactions With the Participation
of Peroxides

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B008/B014

solvent and cannot be separated. When studying the oxidation of phenols with acyl peroxides (Refs. 49, 126-143), the authors found that the reaction is not catalyzed by acids and bases. The reaction rate depends on the nature of the solvent in a very complicated manner. Besides polarity, also the existence of hydrogen bonds appears to be of some importance. For the rules governing this reaction the authors suggested a mechanism according to which benzoyl peroxide and phenol react in the first stage, the slowest one, via the intermediate stage (LXV):



It may be assumed that esters of per acids according to this scheme are also formed in reactions between acyl peroxides and alcohols. This assumption is

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Mechanisms of Some Reactions With the Participation
of Peroxides

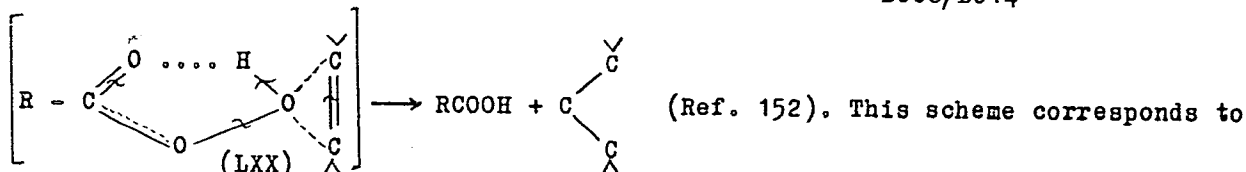
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E008/B014

confirmed by the high yield of corresponding acids. The resulting ester reacts according to either a molecular or a radical mechanism, depending on its structure. Besides molecular and radical reactions also the decomposition of the acyl peroxide itself is possible in the system acyl peroxide - alcohol. The ratio between the contributions of the molecular and the radical processes depends on temperature. The interaction between hydrogen peroxide and olefins may lead to different products, depending on the reaction conditions. (Refs. 10, 89, 90, 144-202). In the dark and without catalyst the reaction usually does not take place. The photosensitized reaction leads to the addition of hydrogen peroxide to the double bond. Besides this addition, decomposition of hydrogen peroxide in water and oxygen as well as oxidative side reactions are observable in this process. Oxidative side reactions proceed in the presence of carboxyl- and other functional groups in the olefin molecule. This reaction is likely to proceed like the hydrogenation of olefins that is catalyzed by acids. α -oxides are formed on interaction between olefins and per acids (reaction according to Prilezhayev - Ref. 147). All experimental data may be explained by means of the transition stage (LXX):

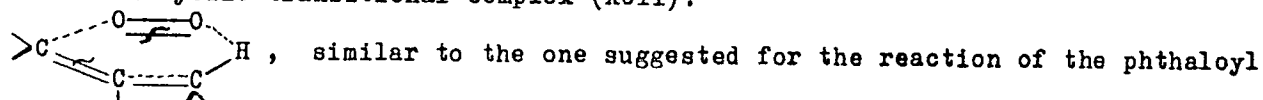
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Mechanisms of Some Reactions With the Participation of Peroxides

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B008/B014



the data on the stereospecificity of the reaction according to Prilezhayev (Ref.153). The relative yields of the oxidation products are obviously dependent on the distribution of electron density in the free radical. The extraordinarily smooth course of this reaction can, however, hardly be explained only by means of the electron effect in the free radical. The reaction probably takes place via a photo-activated cyclic transitional complex (XCII):

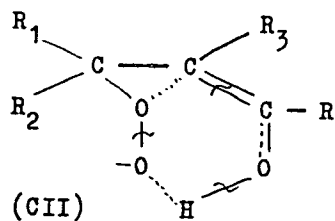


peroxide. A study of the formation of α -oxides in the alkaline oxidation of cis- and trans-benzalacetones, β -methyl trans-benzalacetophenone, and other derivatives with hydrogen peroxide showed that this is not a stereospecific reaction. The data concerning this reaction do not contradict the assumption that it proceeds via an activated complex of the type (CII):

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Mechanisms of Some Reactions With the Participation
of Peroxides

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B008/B014



The following Soviet authors are mentioned: G. D. Lyubarskiy, M. Ya. Kagan, G. A. Razuvayev, V. N. Latyayeva, N. A. Prilezhayev, and O. A. Chaltykyan. There are 1 table and 202 references, 29 of which are Soviet.

Card 7/7

AUTHORS: Kazakova, V. M., Syrkin, Ya. K.,
Corresponding Member AS USSR

S/020/60/131/02/038/071
B004/B007

TITLE: The Hyperfine Structure of the Electron Paramagnetic Resonance
Spectra of Benzophenone-K-ketyl 1

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 2, pp 346 - 347
(USSR)

ABSTRACT: In reference 1, the authors give a report on electron paramagnetic resonance (e.p.r.) spectra of several ketyl reaction products of alkali metals with ketones in an inert gas flow. In the present paper, the hyperfine structure of the e.p.r. spectra of benzophenone-K-ketyl and of phenyl-diphenyl-ketone-K-ketyl in a benzene solution was investigated. Resolution of the hyperfine structure of the last-mentioned compound could not be successfully attained. In the case of benzophenone-K-ketyl a septet was observed (Fig 1), which was resolved into 23 lines when the solution was diluted (Fig 2). The authors give an explanation of the spectrum: The seven components of the spectrum are produced by direct interaction of the unpaired electron with the four ortho- and two paraprotons of the ring. Further cleavage is caused by the four metaprotons. The spin densities of the unpaired electron were calculated as being 0.093 for the o- and

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The Hyperfine Structure of the Electron Paramagnetic
Resonance Spectra of Benzophenone-K-ketyl

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p-position, and 0.031 for the m-position (Fig 3). These values agree well with those obtained for diphenyl methyl (o- and p-position - 0.10). The authors continue investigating the e.p.r. spectra of solutions of aromatic and aliphatic metal ketyls. There are 3 figures and 4 references, 2 of which are Soviet.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im.
M. V. Lomonosova (Moscow Institute of Fine Chemical Technology
imeni M. V. Lomonosov)

SUBMITTED: November 4, 1959

Card 2/2

AUTHORS: Borod'ko, Yu. G., Syrkin, Ya. K.,
Corresponding Member AS USSR

S/020/60/131/04/042/073
B004/P125

TITLE: The Dependence of the Frequencies and Intensities of the Raman
Spectrum Lines of Mixtures of Ketone With Chloroform on Temperature
and Concentration

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 4, pp 868 - 871 (USSR)

TEXT: The scope of this paper was the investigation of the interaction between ketones and chloroform in the formation of molecular compounds. The intensity of the Raman spectrum lines was measured by means of an ISP-51 spectrograph with photoelectric recording. Investigated were: acetone, acetophenone and chloroform dissolved in hexane; as well as acetone, acetophenone, diethyl ketone, and benzophenone dissolved in chloroform at temperatures between -90° and $+30^{\circ}$. Tables 1 and 2 give the integral intensities of the lines, where the intensity of the individual substance with respect to 1 mol at $+30^{\circ}$ is set equal to 100. The intensity of the C=O and C-H lines increases in the system ketone + chloroform and decreases in solutions of these substances in hexane. The intensity of the C-Cl line remains practically constant (Fig 1). The intermolecular interaction is accordingly manifested above all in the C=O bond of the ketone and the C-H bond

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AUTHORS:

Shidlovskaya, A. N., Syrkin, Ya. K., Corresponding Member
AS USSR, Novikov, S. S., Faynzil'berg, A. A.,
Sevost'yanova, V. V., Gulevskaya, V. I.

TITLE:

Dipole Moments of Some Halogen Polynitroalkanes

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 6,
 pp. 1376 - 1377

TEXT: To investigate the effect of an accumulation of nitro groups for polarity and chemical properties, the authors measured the dipole moments of the compounds $\text{CCl}(\text{NO}_2)_3$, $\text{CBr}(\text{NO}_2)_3$, $\text{CI}(\text{NO}_2)_3$, $\text{CH}_3\text{C}(\text{NO}_2)_3$, $\text{CH}_3\text{CH}(\text{NO}_2)_2$, $\text{CH}_3\text{CBr}(\text{NO}_2)_2$, $\text{CH}_3\text{CCl}(\text{NO}_2)_2$, and $\text{CH}_3\text{CHBr}(\text{NO}_2)_2$ in benzene at 25°C by the heterodyne method. Table 1 lists the investigated concentrations of substances, the sum of atomic and electron polarization, and the dipole moments. A comparison of the dipole moments of CH_3X and $\text{CX}(\text{NO}_2)_3$ (X = halogen) shows, for the halogen trinitromethanes, a small negative

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